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# ELECTRICAL CONDUCTIVITY OF WARM DENSE MATTER: ELECTRON JELLIUM—NEW GAS–PLASMA COMPONENT

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**Summary.** An original chemical model of dense metal vapor plasma containing atoms, immersed in electron jellium, as well as free (thermally ionized) electrons and ions is proposed. The main feature of the model is the electron jellium, which exists for any density of atomic component. The number of the jellium electrons increased with compression. The process of its appearance can be called “cold" ionization or ionization by pressure. The composition of the gas-plasma mixture is calculated, including the concentration of the atoms and electrons of the jellium and the concentration of free, thermally ionized electrons and ions. The conductivity of dense vapors is determined by the sum of the conductivity of the thermal electrons, calculated according to the Frost formula, and the conductivity of jellium, calculated according to the Regel–Ioffe formula. At compression, the concentration of thermal electrons decreases and the density of jellium electrons increases. The electrical conductivity passed through the minimum from conductivity of thermal electrons to the conductivity of electrons of jellium, accordingly. Calculations of the electrical conductivity of supercritical metal vapors quite well agree with experimental data.

## 1 INTRODUCTION

High values of metal vapors (Al, Cu, Ni, Fe) conductivity were obtained in experiments [1–3] on pulse explosion of wires at high density and supercritical temperatures ($8000 \leq T \leq 30000$ K). Such condition of substance has been called Warm Dense Matter (WDM). From the theory’s standpoint, the WDM region is difficult because of the high density. The number of atoms increases with increasing of density in the ideal gas, and the ionization degree reduces to zero and gas becomes completely atomic. Conductivity at such process also falls. Experiments [1–3] show decreasing of conductivity with increasing of density at the moderate density. However, at further increase in density, the conductivity decrease stops, and there, after passing through the minimum, its sharp exponential growth observes almost to the metal values. It is possible to speak about the effect of metallization of dense gas (fluid) as conductivity reaches values close to metal ones.

For metal vapors, a sharp increase of the conductivity under vapors compression used to be explained by the “anomalous” Coulomb non-ideality effect on the ionization potentials of atoms and ions [4–6]. It’s leading to a sharp increase in the degree of ionization, up to two and

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three multiple ionization of atoms. The term “anomalous" is used by us because the parameter of Coulomb non-ideality, determined by the relation of Debye energy to temperature, reaches values about several tens. Use of corrections calculated theoretically for a rarefied plasma leads in such circumstances to absurdity [7, 8]. There are different kinds of extrapolation ratios, e.g., Pade approximation [9]. As a result, a three, and sometimes, four-multiple ionization of atoms is surprising at temperatures even lower than 10000 K. The Coulomb’s non-ideality correction stops being the correction as, occasionally, exceeds the contribution of approximation zero term which is the ideal gas of free charges. The decrease in potential of ionization caused by it exceeds the sum of potentials of ionization of atom and its ions and makes tens eV. As for the calculation of momentum relaxation time, which determines the actual conductivity of the substance, the analysis of the approaches shows a low sensitivity of the result to the choice of approximations. Among such options, we can mention the method of moments by Zubarev [4]; the Ziman formula [5] and finally, the simple additive formula of the resistances of atomic and charged components [6].

In this paper, we propose a new, alternative physical model for the metallization of atomic metal vapor under compression. It based on introducing of new electron component—electron jellium. The reason for the jellium appearance in the dense gas is quite simple. Isolated atom occupies the entire space, and the atom surrounded by its kind—only a restricted volume defined by the size of the Wigner–Seitz cell. For this reason, tails of the wave functions of the bound electrons will partially lie outside the Wigner–Seitz cell at any density and therefore belong to all the cells in the system. Electron jellium occurs. When arranging the ion cores, the electron jellium turns into a Bloch conduction electrons. Consistent consideration of this transformation is a complex task for many-body theory. However, sufficiently reliable estimates, at least, for the concentration of electrons of jellium and their contribution to conductivity is possible, and that was done by us earlier in [10] to estimate the conductivity of metal vapor at the critical point.

## 2 THE MAIN RELATIONS

Let us consider the system, consisting of $N_\mathrm{a}$ atoms, $N_\mathrm{i}$ ions, and $N_\mathrm{e}$ electrons in volume $V$ at temperature $T$. Let’s denote the radius of Wigner–Seitz cell for the atomic component as $R_\mathrm{a} = (3V/4\pi N_\mathrm{a})^{1/3}$ and the charged one as $R_\mathrm{i} = (3V/4\pi N_\mathrm{i})^{1/3}$. For the normal density of metal, this radius is $R_0 = (3V/4\pi N_0)^{1/3}$. Helmholtz free energy of such system is written as follows:

$$F = F_\mathrm{a} + F_\mathrm{ch}, \tag{1}$$

where

$$F_{\mathrm{a}} = -N_{\mathrm{a}} k_{\mathrm{B}} T ln \frac{eV g_{\mathrm{a}} \mathrm{e}^{\beta I}}{N_{\mathrm{a}} \lambda_{\mathrm{a}}^3} + N_{\mathrm{a}} k_{\mathrm{B}} T \frac{4\eta - 3\eta^2}{(1-\eta)^2} + \frac{1}{2} N_{\mathrm{a}} E_{\mathrm{coh}}(y_{\mathrm{a}}), \tag{2}$$

$$F_{\mathrm{ch}} = -N_{\mathrm{e}} k_{\mathrm{B}} T ln \frac{eV g_{\mathrm{e}}}{N_{\mathrm{e}} \lambda_{\mathrm{e}}^3} - N_{\mathrm{i}} k_{\mathrm{B}} T ln \frac{eV g_{\mathrm{i}}}{N_{\mathrm{i}} \lambda_{\mathrm{i}}^3} - (N_{\mathrm{e}} + N_{\mathrm{i}}) \Delta f_{\mathrm{ei}}. \tag{3}$$

The first term (2) in free energy (1) just the same as in all our previous works devoted to near-critical region of metals vapors [10–12], where: $k_{\mathrm{B}}$ is the Boltzmann constant; $I$ is the ionization potential of an isolated atom; $\beta = 1/(k_{\mathrm{B}} T)$ is the inverse temperature; $\lambda_{\mathrm{a}}$ is the thermal de-Broglie wavelength of an atom; $g_{\mathrm{e,i,a}}$ are the statistical weights of the correspondent component; $n_{\mathrm{e,i,a}} = N_{\mathrm{e,i,a}}/V$ are the densities of the correspondent component; $\eta = 4/3\pi n_{\mathrm{a}} R_{\mathrm{a}}^3$ is the packing parameter; $E_{\mathrm{coh}}(y_{\mathrm{a}}) = E_{\mathrm{UBER}}(\Delta E, y_0, y_{\mathrm{a}}, B)$ is the cohesive energy [12–14] depending on three parameters: the evaporation heat of metal under normal conditions $\Delta E$, the normal (solid) density $\rho_0$, and the isothermal bulk modulus $B$. Here $y_0 = R_0/a_0$, $y_{\mathrm{a}} = R_{\mathrm{a}}/a_0$ are the solid and current radius of Wigner–Seitz cell expressed in Bohr radius, respectively. $y_{\mathrm{i}} = R_{\mathrm{i}}/a_0$ is the current ion radius of Wigner–Seitz cell in atomic units. $\Delta f_{\mathrm{ei}} \sim \mathrm{e}^2/R_{\mathrm{i}}$ is the contribution due to interaction between electrons and ions in nearest neighbor approximation.

Knowing the density of atoms, we can determine the density of electron jellium $n_{\mathrm{j}} = N_{\mathrm{j}}/V$ via degree of “cold" ionization $\alpha_{\mathrm{j}}$ which tends to a charge of an ionic core in liquid metal

$$n_{\mathrm{j}} = \alpha_{\mathrm{j}} n_{\mathrm{a}}. \tag{4}$$

The methods used for calculation described in [10]. The equilibrium composition of gas-plasma mixture is determined by solving the balance equations, where the primary relation is the equality of the chemical potentials of atoms $\mu_{\mathrm{a}}$, electrons $\mu_{\mathrm{e}}$ and ions $\mu_{\mathrm{i}}$ in ionization reaction.

Entering degree of thermal ionization $\alpha = n_{\mathrm{e,i}}/n$, we will obtain the equation of ionization balance which solution for value $\alpha$ is called the Saha formula:

$$\frac{\alpha^2}{1-\alpha} = n\lambda_{\mathrm{e}}^3 \frac{g_{\mathrm{a}}}{2g_{\mathrm{i}}} exp\left(\beta I - \frac{2\beta Ry}{y_{\mathrm{i}}} - \frac{\beta E_{\mathrm{coh}}(y_{\mathrm{a}})}{2}\left(1 - \frac{y_{\mathrm{a}}}{3E_{\mathrm{coh}}(y_{\mathrm{a}})} - \frac{\mathrm{d}E_{\mathrm{coh}}(y_{\mathrm{a}})}{\mathrm{d}y_{\mathrm{a}}}\right)\right). \tag{5}$$

In (5), $Ry$ is the ionization potential of the hydrogen atom. It is necessary to supplement the Saha equation by two equations of balance: for electroneutrality and nuclei density. The equation (5) completely defines the composition of gas-plasma mixture, and the equation (4) allows to find the density of new components—electron jellium.

## 3 THE DENSITY OF JELLIUM. THE DEGREE OF “COLD” IONIZATION

It is possible to calculate, in cell approximation, that part of the electron density, which participates in the formation of jellium. The wave function of an $i$-th electron $\Psi_i(r)$ of an isolated

atom calculated numerically by the Hartree–Fock method and presented in [15] in the form of expansion of the Slater-type orbitals. In the EAM method, the fraction $\alpha_{\mathrm{HF}}$ determined by integrating the $(\Psi_i(r))^2$ outside the Wigner–Seitz cell and the contribution of the permanent background within the cell $(\Psi_i(y_{\mathrm{a}}))^2$:

$$\alpha^i_{\mathrm{HF}} = \int_{y_{\mathrm{a}}}^{\infty} (\Psi(r))^2 r^2 dr + \frac{y_{\mathrm{a}}^3}{3} (\Psi(y_{\mathrm{a}}))^2. \tag{6}$$

Jellium electron concentration in this calculation defined by the ratio:

$$n_{\mathrm{e}} = \alpha_{\mathrm{HF}} n_{\mathrm{a}}. \tag{7}$$

We will call this variant the “Hartree–Fock".

The density of jellium can also be determined, using results of calculations by the embedded atom method. In [13], these data were processed, generalized and presented in the form of universal scaling dependencies of the atom’s binding energy both on the density of the nuclei and the density of jellium. Based on the equality of these dependencies, a formula was proposed which links a unitless value of the jellium density with the parameter $a^*$:

$$\frac{n_{\mathrm{e}}}{n_{\mathrm{m}}} = (\mathrm{e}^{a^*})^{1/\gamma} = \alpha_{\mathrm{sc}}, \tag{8}$$

where $\gamma = \lambda_{\mathrm{TF}}/l$, $l$ is the scaling length, $\lambda_{\mathrm{TF}}$ is the Thomas–Fermi screening length [14].

Electron concentration in metal at the normal density $n_{\mathrm{m}}$ is the tabular value [16]. As a rule, it can be associated with the effective valence $z_0$ and nuclei density of metal under normal conditions of $n_0$ by the ratio $n_{\mathrm{m}} = n_0 z_0$. A way of calculation of the electron density at the depression of metal nuclei based on the ratio (8) is named in [10] as “scaling".

## 4 CALCULATION OF THE ELECTRICAL CONDUCTIVITY. DISCUSSION OF RESULTS

Electrons of jellium and thermally ionized ones are in different energy intervals. The second ones is in positive energy region, sometimes talk about the ionization continuum. Electrons of jellium have negative energy, but at the same time can propagate in the entire space. Both kinds of electrons are separated by the energy close to atom ionization potential. It is natural to assume that their contribution in total electrical conductivity $\sigma$ of gas-plasma mixture will be additive:

$$\sigma = \sigma_{\mathrm{t}} + \sigma_{\mathrm{j}}. \tag{9}$$

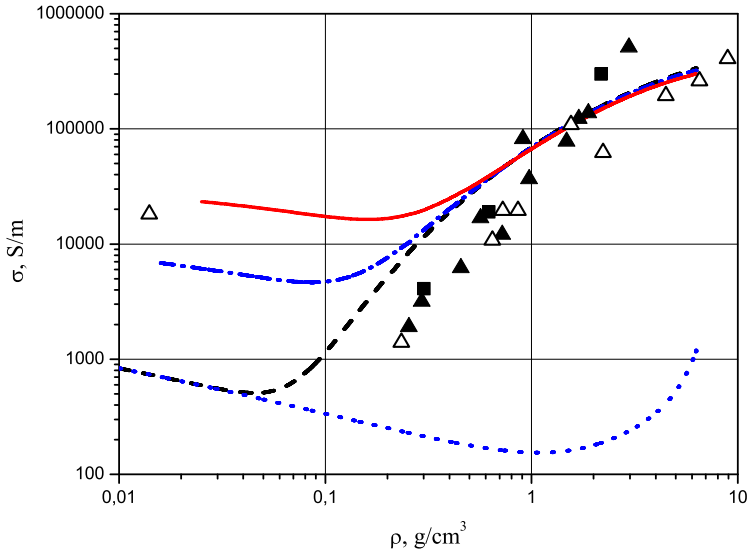


Figure 1: The electrical conductivity of copper on various isotherms. Experiment [2]: ▲—$T = 8000$ K, ■—$T = 16000$ K, △—$T = 30000$ K. This work: dotted line—the contribution of thermal electrons at temperature $T = 8000$ K; dashed, dash-dotted and solid curves—total electrical conductivity at temperatures 8000, 16000 and 30000 K, respectively. The degree of "cold" ionization calculated on "Hartree–Fock".

In (9), $\sigma_t$ is the electrical conductivity due to thermal electrons, and $\sigma_j$ is the electrical conductivity due to electron jellium. For calculation $\sigma_t$, we will use well proved Frost's formula [17].

Jellium electrons also participate in electrical conductivity as they have the opportunity to move from the cell to the cell. It is natural to assume that the path length $l_p$ of the jellium electrons will be of the order of interatomic distance $l_p = 2R_a$. The Regel–Ioffe formula is used for the estimation of the electrical conductivity of jellium:

$$\sigma_j = n_j \frac{q_e^2}{m_e} \tau. \tag{10}$$

In (10), $n_j$ is the density of jellium electrons, $\tau$ is the mean free time, that is equal to transit flight time of internuclear distance $l_p$ ($2y$ in atomic units) with Fermi velocity $v_F = p_F/m_e$:

$$\frac{\tau}{m_e} = \frac{2R_a}{p_F}, \tag{11}$$

where $p_F = (3\pi^2 n_j)^{1/3}\hbar$ is the Fermi momentum.

Within the proposed model we calculated electrical conductivity of metal vapors on isotherms in the range of temperatures $T = 8000$–$30000$ K for Al, Cu, Fe, and Ni. Calculation of differ-

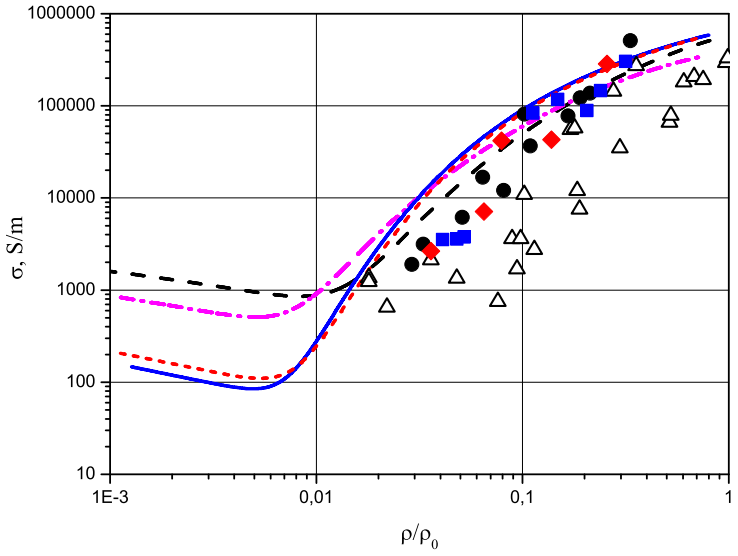


Figure 2: The electrical conductivity on reduced density ($\rho_0$—solid state density for metal) for Al, Cu, Fe, Ni at $T = 8000$ K. Experiment [2]: ● —Cu, ■—Fe, ♦—Ni, △—Al. This work: dashed curve—Al, dash-dotted curve—Cu, solid curve—Fe, dotted curve—Ni. The degree of "cold" ionization calculated on "Hartree–Fock".

ent isotherms of copper presented in figure 1. At the small density calculations naturally differ since, at the low density, conductivity depends on the concentration of the thermal electrons, according to the Saha formula. With density increase the electrical conductivity passes through the minimum, then there is the sharp growth of conductivity to the values close to metal ones. Figure 1 shows that at the large density the isotherms are almost indiscernible that corresponds to experimentally measured values. In our model, the independence of the asymptotic on temperature is explained by its tend at the large density to the conductivity values of jellium (10), that is not temperature-dependent. Figure 2 presented the dependence of electrical conductivity on the reduced density for Al, Cu, Fe, Ni for the near-critical isotherm $T = 8000$ K. At density increase, calculation results for different metals are close to each other. It once again shows that with density increase jellium electrons begin to play the major role. Dependence of conductivity on temperature practically disappears, and dependence on density becomes exponential on the particular interval. The sharp rise of conductivity is associated with the exponential dependence of electron density of the bound electrons on distance. Comparison with experimental data gives a base to conclude the emergence of new electron component and its possible co-existence along with the traditional one.

## 5 CONCLUSIONS

The physical model of dense metal vapors (fluid) is proposed. For the first time, jellium is considered as an additional component. Jellium is the result of the compression of an atomic gas. The composition of the plasma of metal vapors is calculated on the assumption of independence of atomic and ionized components. The Frost's formula is used for calculation of the electrical conductivity of thermally ionized electrons and the Regel–Ioffe formula for the conductivity of jellium. The electrical conductivity of dense metal vapors is calculated along isotherms up to conditions of the supercritical fluid. The presented comparison with the available experimental data shows reasonableness of the proposed model and, to some degree, confirms the hypothesis about the existence of jellium in dense atomic gas.

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